

## **Coordination Chemistry of Actinides with Sulfur Donor Ligands**

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Separation of the actinides Am and Cm from the trivalent lanthanide cations in used nuclear fuel is an important component of advanced concepts for nuclear power generation and waste disposal. However, the great chemical similarity of trivalent Am and Cm and the light lanthanide elements makes the separation difficult. We have been studying the lanthanide and actinide coordination chemistry of the most effective separations reagent, bisalkyldithiophosphinic acids, to understand the origin of their great selectivity for Am and Cm over the lanthanides. Our previous optical, X-ray, and neutron measurements showed that three bisalkyldithiophosphinate molecules acids bind each metal, for both the lanthanides and actinides. These results did not agree with the published interpretations of the thermodynamic data for these compounds, which implied the presence of four bisalkyldithiophosphinate molecules around each metal cation. Using NMR, we showed that interactions between uncomplexed bisalkyldithiophosphinic acid molecules are weaker than others had hypothesized. Applying this correction, the thermodynamic data now implies the presence of three bisalkyldithiophosphinate molecules around each metal cation, in agreement with our spectroscopic data. Further analysis of the X-ray data also shows no significant difference in the metal *d*-orbital population of the lanthanides and actinide complexes, eliminating one possible source of the ligand's preference for the actinides.